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(54) Dishwashing Detergents Containing a Biologically Degradable Builder Component

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(54) Title: DISHWASHER AGENT WITH BIODEGRADABLE BUILDERS

(54) Bezeichnung: GESCHIRRSPÜLMITTEL MIT BIOLOGISCH ABBAUBARER BUILDERKOMPONENTE

(57) Abstract

The invention concerns low-alkaline agents for use in dishwashing machines, the agents containing builders which are readily biodegradable. These readily biodegradable builders are copolymers of [meth]acrylic acid or [meth]acrylate, maleic acid or maleate and vinyl alcohol and/or vinyl acetate.

(57) Zusammenfassung

Die Erfindung betrifft niederalkalische Mittel zum maschinellen Reinigen von Geschirr, die biologisch gut abbaubare Builderkomponenten enthalten. Die biologisch gut abbaubaren Builderkomponenten sind Copolymere, die aus (Meth)acrylsäure bzw. (Meth)acrylat, Maleinsäure bzw. Maleat und Vinylalkohol und/oder Vinylacetat aufgebaut sind.

Dishwashing detergents containing a biologically degradable builder component

This invention relates to low-alkali dishwashing detergents for dishwashing machines containing a biologically degradable builder component.

In addition to oxygen-based bleaching agents, surfactants and enzymes, low-alkali machine dishwashing detergents of the latest generation contain a combination of water-soluble builders consisting of complexing agents, for example citrate, alkali carriers, for example soda, hydrogen carbonate or disilicate, and dispersants, for example polycarboxylates. Other possible builder components are organophosphonic acids, aminocarboxylic acids or crystalline layer silicates. The phosphates previously used, for example pentasodium tripolyphosphate, are now being phased out on ecological grounds.

The polycarboxylates, for example maleate/acrylate copolymers, used in modern detergents prevent the formation of lime coatings in the presence of excessive residual water hardness in the main wash and final rinse cycles. In addition, they improve the clear rinse effect at high salt concentrations in the wash liquor.

The disadvantage of these polycarboxylates is that they are not readily biodegradable. Accordingly, there is a need for machine dishwashing detergents which contain biodegradable builder components, but which at the same time have the established performance spectrum of modern dishwashing detergents. Although many readily biodegradable builder components, such as for example oxidized starch or polyaspartic acid, have a good dispersing effect on precipitated calcium carbonate, they are poor complexing agents for water hardness.

US 3,887,480 discloses dishwashing and laundry

detergents which contain a polymer consisting of 35 to 70 mole-% of maleic acid, 20 to 45 mole-% of vinyl acetate and 2 to 40 mole-% of acrylic acid. **EP 0 193 360 B1** describes zeolite-containing laundry detergents containing polycarboxylate polymers produced from a C_{3-10} monocarboxylic acid, a C_{4-6} dicarboxylic acid and a nonionic spacer, for example vinyl alcohol. **US 3,755,264** discloses copolymers produced, for example, from 85 to 99 mole-% of maleic anhydride and 1 to 15 mole-% of a mixture of acrylic acid and vinyl acetate. **EP 0 076 992 A1** discloses inter alia the use of polymers produced from 50 to 95% by weight of acrylic acid, 0.5 to 5% by weight of vinyl acetate and up to 49% by weight of maleic acid as incrustation inhibitors in detergents.

It has now surprisingly been found that copolymers produced from (meth)acrylic acid or (meth)acrylate, maleic acid or maleate and vinyl alcohol and/or vinyl acetate in certain quantity ratios not described in the documents cited above are eminently suitable for use as builder components in machine dishwashing detergents.

The present invention relates to a low-alkali machine dishwashing detergent of which a 1% by weight aqueous solution has a pH value of 8 to 11.5 and preferably 9 to 10.5 and which contains water-soluble builder components and oxygen-based bleaching agents, characterized in that it contains as the water-soluble builder component a copolymer of which 60 to 95% by weight and preferably 70 to 90% by weight consists of (meth)acrylic acid or (meth)acrylate, preferably acrylic acid or acrylate, and maleic acid or maleate and 5 to 40% by weight and preferably 10 to 25% by weight of vinyl alcohol and/or vinyl acetate, the ratio by weight of (meth)acrylic acid or (meth)acrylate to maleic acid or maleate being from 1.5:1 to 4:1 and preferably from 2:1 to 2.5:1, both the quantities and the ratios by weight

being based on the acids and a copolymer of the salts of the acids and vinyl alcohol being preferred.

The copolymers used in accordance with the invention may be produced by any of the known and usual processes. More particularly, (meth)acrylic acid, preferably acrylic acid, and maleic acid are reacted with vinyl alcohol and/or vinyl acetate, after which the acids are optionally neutralized, preferably to their alkali metal salts, such as the sodium or potassium salts, or ammonium salts or alkanolamine salts, such as the monoethanolamine salt or the triethanolamine salt, and the vinyl acetate is optionally partly or completely decomposed into vinyl alcohol.

Similarly to the known (co)polymeric polycarboxylic acids or polycarboxylates, such as homopolymeric or copolymeric acrylic acids or acrylates, copolymers which are either completely or at least partly neutralized, more particularly to more than 50%, based on the carboxyl groups present, are also preferred. A particularly preferred copolymer is a completely neutralized copolymer, i.e. a copolymer consisting of the salts of (meth)-acrylic acid, preferably acrylic acid, and maleic acid, more particularly the sodium or potassium salts, and vinyl alcohol. The copolymers generally have a relative molecular weight in the range from 1,000 to 200,000, preferably in the range from 2,000 to 50,000 and more preferably in the range from 3,000 to 10,000. They are preferably used in the form of spray-dried powders. Particularly preferred copolymers are produced by the process described in earlier German patent application P 43 00 772.4.

Preferred dishwashing detergents according to the invention contain the copolymer in quantities of 0.5 to 30% by weight and preferably in quantities of 2 to 20% by weight and also contain 0.5 to 20% by weight and prefer-

ably 5 to 15% by weight of an oxygen-based bleaching agent, more particularly alkali metal perborate and/or percarbonate, and nonionic surfactants in a quantity of at most 5% by weight and preferably at most 2% by weight, the detergents being free from anionic, cationic or amphoteric surfactants.

In one preferred embodiment, alkali metal carbonates and/or hydrogen carbonates, more particularly the sodium salts, are present as alkali carriers in a quantity of up to 60% by weight and preferably in a quantity of 5 to 50% by weight.

The dishwashing detergents according to the invention may contain other water-soluble builder components, for example synthetic polymers which are understood to be the salts of polymerization products of unsaturated carboxylic acids and which include, for example, polyacrylates, polymethacrylates, polymaleates or copolymers of acrylic acid with maleic acid or maleic anhydride, in a quantity of 0.5 to 30% by weight and preferably in a quantity of 2 to 20% by weight. Suitable polyacrylates are, for example, Alcosperse® 102, 104, 106, 404, 406, products of Alco; Acrysols® A N1, LMW 45 N, LMW 10 N, products of Norsohaas; Degapas®, a product of Degussa AG. Suitable copolymers of polyacrylic acid and maleic acid are, for example, Sokalan® CP 5, SP 7, products of BASF; Acrysol® QR 1014, a product of Norsohaas; Alcosperse® 175, a product of Alco. In principle, phosphates or zeolites may also be present, although the dishwashing detergents are preferably free from zeolites and phosphate-containing builder components.

The foaming behavior of the surfactants suitable for use in the detergents according to the invention is a key factor. In view of the mechanics of dishwashing machines, low-foaming compounds are preferred. These are, above all, nonionic surfactants. Accordingly, the

dishwashing detergents according to the invention are preferably free from anionic, cationic or amphoteric surfactants. The nonionic surfactant content is at most 5% by weight and preferably at most 2% by weight. Suitable nonionic surfactants are, above all, adducts of 1 to 20 moles of ethylene oxide (EO) and/or 1 to 20 moles of propylene oxide (PO) with 1 mole of an aliphatic compound containing 10 to 20 carbon atoms from the group of alcohols, carboxylic acids, fatty amines, carboxylic acid amides and alkane sulfonamides. In addition to the water-soluble nonionic surfactants, however, water-insoluble or substantially water-insoluble polyglycol ethers containing 2 to 7 ethylene glycol ether groups in the molecule are also important and are preferably used in combination with water-soluble nonionic surfactants. In addition, alkyl polyglycosides corresponding to the general formula $R-O-(G)_x$, where R is a primary, linear or branched aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms, G is a glycose unit containing 5 or 6 carbon atoms and the degree of oligomerization x is between 1 and 10, may also be used as nonionic surfactants.

Preferred dishwashing detergents according to the invention additionally contain complexing agents from the group of dibasic and polybasic organic carboxylic acids and salts thereof, for example nitrilotriacetic acid, but especially citric acid or salts thereof, in a quantity of 0.5 to 60% by weight and preferably in a quantity of 20 to 50% by weight.

Typical alkalizing agents used in low-alkali machine dishwashing detergents include alkali metal carbonates and hydrogen carbonates and alkali metal silicates with an $SiO_2:M_2O$ (M = alkali metal atom) molar ratio of 1.5:1 to 2.5:1. The alkali metal carbonates and hydrogen carbonates preferably used in the detergents according to

the invention are the sodium carbonates and hydrogen carbonates which are present in the quantities mentioned above. The high-alkali metasilicates are preferably not used as alkali carriers. Instead of the metasilicates, alkali metal silicates, preferably sodium silicates with a molar $SiO_2:Na_2O$ ratio of 1.5:1 to 2.5:1, are preferably used in quantities of up to 30% by weight and, more preferably, in quantities of 5 to 20% by weight, based on the dishwashing detergent as a whole.

Among the compounds used as oxygen-based bleaching agents, sodium perborate tetrahydrate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$), sodium perborate monohydrate ($NaBO_2 \cdot H_2O_2$) and the peroxycarbonate ($Na_2CO_3 \cdot 1.5\ H_2O_2$) are particularly important. Other useful bleaching agents are, for example, peracidic salts of organic acids, such as perbenzoates, or salts of diperdodecanedioic acid. The detergents preferably contain 0.5 to 20% by weight and, more preferably, 5 to 15% by weight of an oxygen-based bleaching agent, more particularly alkali metal perborates and/or percarbonates. Moreover, the addition of small quantities of known bleach stabilizers, such as borates or metaborates and metasilicates and also magnesium salts, for example, magnesium sulfate, can be useful.

Suitable bleach activators for these oxidizing agents are, in particular, N-acyl and O-acyl compounds, preferably tetraacylated diamines, such as N,N,N',N'-tetraacetyl ethylenediamine (TAED). The detergents according to the invention contain these typical bleach activators in a quantity of 0.1 to 10% by weight and preferably in a quantity of 1 to 5% by weight. The detergents according to the invention are preferably free from active chlorine donors, such as trichloroisocyanuric acid for example.

To improve the removal of protein- or starch-containing food residues, the detergents may contain en-

zymes, such as proteases, amylases, lipases or cellulases, for example proteases, such as BLAP® 140, a product of Henkel KGaA, Optimase® M-440, Optimase® M-330, Opticlean® M-375, Opticlean® M-250, products of Solvay Enzymes; Maxacal® CX 450.000, Maxapem®, products of Ibis; Savinase® 4.0 T, 6.0 T, 8.0 T, products of Novo; or Experase® T, a product of Ibis; amylases, such as Termamyl® 60 T, 90 T, products of Novo; Amylase-LT®, a product of Solvay Enzymes; or Maxamyl® P 5000, CXT 5000 or CXT 2900, products of Ibis; lipases, such as Lipolase® 30 T, a product of Novo; cellulases, such as Celluzym® 0.7 T, a product of Novo Nordisk. Enzymes may be present in the detergents according to the invention in a quantity of 0.1 to 5% by weight and preferably in a quantity of 0.5 to 2% by weight, based on the dishwashing detergent as a whole.

To prevent the tarnishing of silver tableware, so-called silver protectives of the type described in earlier German patent application P 43 15 397.6, more particularly water-soluble Mn(II) salts, may optionally be present in a quantity of up to 2% by weight and preferably in a quantity of 0.1 to 0.5% by weight.

The dishwashing detergents according to the invention are preferably present in the form of powder-form, granular or tablet-form preparations which may be produced by methods known per se, for example by mixing, granulation, roll compacting and/or by spray drying. The polymers used in accordance with the invention may also be employed in the form of a compound to be added to other granular constituents of the detergents.

To produce the detergents according to the invention in tablet form, all the constituents are preferably mixed together in a mixer and the resulting mixture is tabletted in conventional tablet presses, for example eccentric presses or rotary presses, under pressures of $200 \cdot 10^5$ Pa

to $1500 \cdot 10^5$ Pa. Breaking-resistant tablets which still dissolve sufficiently quickly under in-use conditions with flexural strengths of normally above 150 N are readily obtained in this way. A tablet produced in this way preferably has a weight of 15 g to 40 g and, more particularly, 20 g to 30 g for a diameter of 35 mm to 40 mm.

The production of the machine dishwashing detergents in the form of non-dust-emitting, storage-stable free-flowing powders and/or granules with high apparent densities preferably in the range from 800 to 900 g/l is carried out, for example, by mixing the builder components with at least part of the liquid mixture components in a first stage of the process, the apparent density of the premix being increased, and then combining the other constituents of the machine dishwashing detergent with the premix thus obtained, if desired after intermediate drying.

Since the alkali metal carbonate content has a considerable bearing on the alkalinity of the product, the intermediate drying step should be carried out in such a way that decomposition of the sodium bicarbonate to sodium carbonate is kept to a minimum (or at least substantially constant). This is because any sodium carbonate additionally formed as a result of drying would have to be taken into consideration in the formulation of the granules. Low drying temperatures not only counteract the decomposition of sodium bicarbonate, they also increase the solubility of the granulated detergent in use. Accordingly, the intermediate drying step is advantageously carried out at a feed air temperature which, on the one hand, should be as low as possible to avoid decomposition of the bicarbonate but which, on the other hand, should be as high as necessary to obtain a product with good storage properties. The drying step is

preferably carried out at a feed air temperature of around 80°C. The granules themselves should not be heated to temperatures above about 60°C.

In the first stage of the mixing process, the builder is exposed to the liquid components generally in the form of a mixture with at least one other component of the dishwashing detergent. This may be done, for example, in a preliminary stage in which the builder component is exposed to and thoroughly mixed with the liquid nonionic surfactants and/or the solution of fragrances in the form of a mixture with perborate. The remaining components are then added and the mixture as a whole is compounded and homogenized in the mixer. There is generally no need to use additional quantities of liquid, i.e. additional water. The mixture obtained is a free-flowing, non-dust-emitting powder with the required high apparent densities in the range from about 800 to 900 g/l.

The preliminary granules are then mixed with the missing components of the dishwashing detergent to form the end product. In all the cases illustrated here, the mixing time both in the preliminary stage of compacting mixing in the presence of liquid components and in the following final mixing phase with the other components is of the order of a few minutes, for example 1 to 5 minutes.

In one particular embodiment, it can be useful in the production of fine granules to subject the granules formed to further stabilization and equalization by dusting their surfaces with powder. Small amounts of waterglass powder or powder-form alkali metal carbonate are particularly suitable for this purpose.

The machine dishwashing detergents according to the invention represent products which, apart from their better biodegradability, are superior to conventional

modern dishwashing detergents above all in regard to bloom inhibition and the clear rinse effect on glasses and knifes.

The following Examples are intended to illustrate the invention without limiting it in any way.

Examples

Granular dishwashing detergents with the following composition (detergent A according to the invention, comparison detergent B and detergent C according to the invention) were produced.

Detergent A contained 10% by weight of the copolymer which had been produced in accordance with the disclosure of earlier German patent application P 43 00 772.4 from 80% by weight of acrylic acid and maleic acid in a ratio by weight of 7:3 and from 20% by weight of vinyl acetate and then completely neutralized.

Comparison Example B contained 10% by weight of an acrylate/maleate copolymer marketed by BASF under the name of Sokalan® CP5.

	A % by weight	B % by weight	C % by weight
Na Citrate	30.0	30.0	40.0
Sokalan CP5	---	10.0	---
Above-mentioned copolymer	10.0	---	5.0
Na_2CO_3	13.0	13.0	6.0
$NaHCO_3$	35.5	35.5	30.1
Na Perborate	5.0	5.0	---
Na Percarbonate	---	---	12.0
TAED	2.0	2.0	3.0
Amylase	1.5	1.5	1.0
Protease	1.5	1.5	1.0
Plurafac LF403 of BASF ($C_{12/18}$ Fatty alcohol·EO·4PO)	0.9	0.9	0.9
Perfume oil	0.6	0.6	0.6
$MnSO_4$	---	---	0.4

Cleaning performance

The **cleaning performance** of detergents A and B was tested in a Miele G 531 dishwashing machine (program: universal, 65°C) with dosages of 30 g in 7.0 l of water (16°dH) in the main wash cycle (soil types as described in **Th. Altenschöpfer, SÖFW, 98 (1972), 763 - 756,** namely: tea, milk, minced meat, pudding, lipstick, starch, oat flakes).

Detergent A according to the invention was superior in its cleaning performance to comparison detergent B, particularly in regard to the removal of starch, minced meat, lipstick and oat flakes and, more particularly, in regard to the removal of tea stains.

Bloom inhibition

The bloom forming effect of detergents A and B was

tested in a Miele G 590 dishwashing machine (program: universal, 65°C) with dosages of 20 g in 7.0 l of water (16°dH) containing 50 g of added pumpable soils (mixture of ketchup, gravy, mustard, potato starch, egg yolk, milk, margarine) in the presence of 3.0 ml of a commercially available rinse aid over 10 wash cycles. The clear rinse effect ("spotting") was evaluated on a scale of 1 (= very poor clear rinse effect) to 8 (= very good clear rinse effect, no water stains). The results of the clear rinse effects obtained with detergent A according to the invention and comparison detergent B on glasses, knifes and china plates are shown in Table 1.

Table 1

	A	B
Glasses	5	1
Knifes	5	3
China plates	5	6

It can be seen that detergent A according to the invention is superior to comparison detergent B above all in regard to the clear rinse effect on glasses and knifes.

Detergent C according to the invention was comparable with detergent A according to the invention in its cleaning performance and bloom inhibiting effect. By virtue of the presence of $MnSO_4$, it showed superior properties above all in regard to preventing the tarnishing of silverware.

CLAIMS

1. A low-alkali machine dishwashing detergent of which a 1% by weight aqueous solution has a pH value of 8 to 11.5 and preferably 9 to 10.5 and which contains water-soluble builder components and oxygen-based bleaching agents, characterized in that it contains as the water-soluble builder component a copolymer of which 60 to 95% by weight and preferably 70 to 90% by weight consists of (meth)acrylic acid or (meth)acrylate, preferably acrylic acid or acrylate, and maleic acid or maleate and 5 to 40% by weight and preferably 10 to 25% by weight of vinyl alcohol and/or vinyl acetate, the ratio by weight of (meth)acrylic acid or (meth)acrylate to maleic acid or maleate being from 1.5:1 to 4:1 and preferably from 2:1 to 2.5:1, both the quantities and the ratios by weight being based on the acids and a copolymer of the salts of the acids and vinyl alcohol being preferred.

2. A detergent as claimed in claim 1, characterized in that it contains 0.5 to 30% by weight and preferably 2 to 20% by weight of copolymer and 0.5 to 20% by weight and preferably 5 to 15% by weight of an oxygen-based bleaching agent, more particularly alkali metal perborate and/or percarbonate, and in that it is free from anionic, cationic or amphoteric surfactants, the nonionic surfactant content being at most 5% by weight and preferably at most 2% by weight, based on the detergent as a whole.

3. A detergent as claimed in claims 1 and 2, characterized in that it contains up to 60% by weight and preferably 5 to 50% by weight of alkali metal carbonate and/or hydrogen carbonate.

4. A detergent as claimed in claims 1 to 3, characterized in that it contains complexing agents from the group of dibasic and polybasic organic carboxylic acids or salts thereof, more particularly citric acid or salts thereof, in a quantity of 0.5 to 60% by weight and

preferably in a quantity of 20 to 50% by weight, based on the detergent as a whole.

5. A detergent as claimed in claims 1 to 4, characterized in that it contains up to 30% by weight and preferably 5 to 20% by weight, based on the detergent as a whole, of alkali metal silicate with an $SiO_2:M_2O$ (M = alkali metal atom) molar ratio of 1.5:1 to 2.5:1.

6. A detergent as claimed in claims 1 to 5, characterized in that it is free from active chlorine donors.

7. A detergent as claimed in claims 1 to 6, characterized in that it contains enzymes in a quantity of 0.1 to 5% by weight and preferably 0.5 to 2% by weight, based on the detergent as a whole.

8. A tablet-form detergent as claimed in claims 1 to 7, characterized in that it is obtainable by mixing all of its constituents in a mixer and tabletting the resulting mixture in a tablet press under pressures of $2 \cdot 10^7$ Pa to $1.5 \cdot 10^8$ Pa.

9. A powder-form or granular detergent as claimed in claims 1 to 7, characterized in that it has an apparent density of 750 g/l to 1000 g/l.

10. The use of the detergent claimed in any of claims 1 to 9 for machine dishwashing.